

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 683 029 B1

(12)

EUROPEAN PATENT SPECIFICATION

F/

(45) Date of publication and mention
of the grant of the patent:
31.07.2002 Bulletin 2002/31

(51) Int Cl.7: B29C 49/64, B29C 49/16
// B29K467:00

(21) Application number: 95303260.4

(22) Date of filing: 16.05.1995

(54) **Biaxially-drawn blow-molded container having excellent heat resistance and method for producing the same**

Biaxial gestreckter, blasgeformter Behälter mit ausgezeichneter Wärmebeständigkeit und Verfahren zu seiner Herstellung

Récipient étiré biaxialement et moulé par soufflage ayant une excellente résistance à la chaleur et procédé de production

(84) Designated Contracting States:
FR GB IT

(30) Priority: 16.05.1994 JP 10036594

(43) Date of publication of application:
22.11.1995 Bulletin 1995/47

(73) Proprietor: TOYO SEIKAN KAISHA LIMITED
Tokyo (JP)

(72) Inventors:

- Nakamaki, Setsuko
Yokohama-shi, Kanagawa-ken (JP)
- Maruhashi, Yoshitsugu
Yokohama-shi, Kanagawa-ken (JP)
- Kato, Nobuyuki
Yokohama-shi, Kanagawa-ken (JP)

- Matsuno, Kenji
Yokohama-shi, Kanagawa-ken (JP)
- Kurashima, Hideo
Yokosuka-shi, Kanagawa-ken (JP)
- Ikegami, Hiroo
Sagamihara-shi, Kanagawa-ken (JP)
- Takeuchi, Kimio
Kawasaki-shi, Kanagawa-ken (JP)

(74) Representative: Bailey, David Martin et al
Brookes Batchellor
102-108 Clerkenwell Road
London EC1M 5SA (GB)

(56) References cited:

EP-A- 0 237 459	EP-A- 0 425 360
EP-A- 0 559 103	EP-A- 0 571 262
EP-A- 0 637 499	US-A- 4 035 455
US-A- 5 378 421	

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

BEST AVAILABLE COPY

EP 0 683 029 B1

Description

BACKGROUND OF THE INVENTION

(1) Field of the Invention

[0001] The present invention relates to a biaxially-stretch-blow-molded container and to a method of producing the same. More specifically, the invention relates to a heat-resistant polyester bottle of the one-piece type having excellent strength in the bottom portion, heat resistance, symmetrical panel-sinking stability in the vacuum pressure and self-standing stability and to a method of producing the same.

(2) Description of the Prior Art

[0002] Biaxially-stretch-blow-molded containers of a thermoplastic polyester such as polyethylene terephthalate (PET) have excellent transparency and luster on the surface, as well as excellent shock resistance, rigidity and gas barrier property that are required for the bottles, and have been used as containers, i.e., bottles for containing a variety of kinds of liquids.

[0003] A hot filling method has been employed for bottling or packaging the contents maintaining enhanced preservability. Therefore, the containers must have heat resistance to withstand high-temperature liquids that are filled therein or the heat treatment that is carried out to sterilize the contents.

[0004] Heat-resistant containers are usually produced by a single-stage blow-molding method in which the blow-molded products and molded products are heated and crystallized, i.e., heat-set, using a single metal mold. With this single-stage blow-molding method, it is difficult to heat-set the recessed bottom portions of ordinary molded articles. To guarantee heat resistance, the recessed bottom portion must have an increased thickness and a complex shape. Accordingly, the weight of the bottom portion is subject to increase.

[0005] There has also been known a two-stage blow-molding method comprising a step for primarily blow-molding a preform article using a metal mold, and a step for finally molding the article by subjecting the article to secondary blow-molding using a metal mold after the article is heat-shrunk via a so-called heat-set step through which the article is heated, shrunk and crystallized in an oven or the like.

[0006] In the two-stage blow-molding method, the article is drawn through the step of primary blow-molding to a sufficient degree at a drawing ratio of 2 to 6 times, and the thus drawn secondarily article is sufficiently shrunk by about 60 to 90% through the heat-set step, in order to improve rigidity of the bottle and to impart heat resistance based upon the intermediate heating. Therefore, the two-stage blow-molding method is suited for producing heat resistant containers.

[0007] Employment of the two-stage blow-molding method has been disclosed in, for example, Japanese Laid-Open Patent Publication No. 205124/1991 according to which a secondary article having a semi-spherical bottom portion is formed by the primary blow molding, the article is then heated in an oven, and the article is subjected to the secondary blow-molding to obtain a final article having a bottom of which the central portion is recessed inwardly of the container.

[0008] According to Japanese Laid-Open Patent Publication No. 189224/1988, furthermore, a secondary article is formed having a semi-spherical bottom formed by the primary blow molding, the bottom is then inverted to form a tertiary article having the bottom of which the central portion is recessed inwardly of the container, the tertiary article as a whole is heated relatively uniformly and is shrunk and, then, the article is subjected to the secondary blow molding to obtain a finally molded-article.

[0009] According to the conventional two-stage blow-molding method, however, if some part is drawn at a large ratio in the final secondary blow molding step, then, the thickness of that part is locally decreased to lose strength or the degree of crystallization is decreased making it difficult to obtain heat resistance.

[0010] That is according to the former prior art, the drawing ratio increases at the bottom corner portion at the time when the secondary article having a semi-spherical bottom portion is subjected to the secondary blowing to obtain a final product having the bottom portion that is inwardly recessed. Therefore, the thickness of the corner portion decreases and the degree of crystallization decreases resulting in a decrease in the strength and heat resistance at that portion.

[0011] According to the latter prior art, a semi-spherical bottom shape is obtained by the primary blow-molding and is inverted to obtain a secondary article having the bottom which is inwardly recessed. At this moment, the whole secondary article is heated relatively uniformly so that the height thereof is shrunk to be smaller than the size of the metal mold for secondary blow molding. In this case, however, the diameter of the barrel is extremely shrunk and when the heat-molded article having a small barrel diameter is subjected to the secondary blowing, the drawing ratio increases at the bottom corner portion to lose heat resistance and strength.

[0012] Moreover, when the heat-resistant container having a thick bottom portion of a recessed shape is obtained

by the two-stage blow-molding method, the bottom of the secondary article formed by primary blow molding has a thick recessed shape like that of the final product. When the bottom portion is heated like the barrel portion, the temperature rises slowly in the thick portion having a large heat capacity and portions other than thick portions are particularly heated. When the thus heated secondary article is subjected to the secondary blow molding, only those thin portions heated at a high temperature are drawn. In particular, the thickness of the bottom corner portion is extremely reduced, which is not desirable. Even when it is attempted to selectively heat thick portions of the bottom, the thick portions that are drawn at a small ratio in the primary blow molding are whitened. Usually, therefore, a complex heating system has been employed according to which the whole bottom portion of the secondary article is maintained at a moldable temperature without substantially causing it to shrink, and the barrel portion is chiefly heated, shrunk and crystallized.

[0013] When the thickness of the bottom portion is increased as described above, there arise problems in that a complex system is required for heat-treating the secondary article and that the weight increases accompanying an increase in the thickness of the bottom portion. It therefore becomes necessary to solve such problems.

[0014] In order to prevent deformation of the bottle caused by the vacuum pressure after the heat-resistant bottle is filled with hot content, furthermore, a panel-rib structure has been widely employed in the barrel portion of the containers. In the container forming such a panel-rib structure in the barrel portion, the panel portion undergoes a paneling deformation inwardly by vacuum pressure. When the bottle is filled with hot content, however, the panel swells outwardly. Once the panel swells outwardly at the time of filling the content, the panel then loses its function to undergo paneling deformation inwardly. Therefore, the panel at the barrel portion is sometimes deformed asymmetrically.

[0015] According to the above-mentioned prior art, the bottle is greatly oriented on the inner side. Moreover, since use is made of a metal mold of a high temperature, the degree of heat set (degree of orientation and crystallization) increases on the outside of the bottle. When the bottle is filled with hot content, therefore, the panel portion swells out under certain circumstances.

[0016] EP 559 103 describes a method of producing a biaxially-stretch blow molded container and a container obtained by the method. A cylindrical preform article is subjected to primary blow molding to obtain a biaxially drawn secondary article. This article is heated to shrink it. The base is cooled and the article is then subjected to secondary blow molding in a cavity mold to produce a finally formed article.

[0017] US 4035455 describes a method for blow moulding a hollow plastic article having a concave base by inward deformation of a portion of the base of a blow-moulded hollow plastics body whilst the base is still warm from the blow-moulding process or with separate re-heating.

SUMMARY OF THE INVENTION

[0018] The object of the present invention therefore is to provide a method of producing a biaxially-stretch-blow-molded container relying upon the two-stage blow-molding by heat-shrinking a secondary article drawn by the primary blow molding into a more desirable form and then subjecting it to the secondary blow molding, without employing complex heating system.

[0019] Another object of the present invention is to provide a one-piece polyester bottle having excellent mechanical strength in the bottom portion, heat resistance, symmetrical panel-sinking stability in the vacuum pressure and self-standing stability in combination, the one-piece polyester bottle capable of being filled with hot content, and a method of producing the same.

[0020] According to a first embodiment of the present invention, there is provided a method of producing a biaxially-stretch-blow-molded container by blow-molding a cylindrical preform article with bottom that is heated at a drawing temperature, comprising:

- a step for subjecting the preform article to the primary blow molding to obtain a biaxially drawn secondary article having a domed bottom portion without substantially containing undrawn portions;
- a step for heating the domed bottom portion of the secondary article to preferentially shrink the bottom portion in order to obtain a tertiary article having a flat bottom portion;
- a step for heating the tertiary article inclusive of the bottom portion and the barrel portion thereof in order to obtain a quaternary article of which the barrel portion is chiefly shrunk; and
- a step for subjecting the quaternary article that is heated to the secondary blow molding to obtain a final container.

[0021] According to a second embodiment of the present invention, there is provided a method of producing a biaxially-stretch-blow-molded container by blow-molding a cylindrical preform article with bottom that is heated at a drawing temperature, comprising:

- a step for subjecting the preform article to the primary blow molding to obtain a biaxially drawn secondary article

having a domed bottom portion with an undrawn thick portion at the center of the bottom, the thick portion being slightly recessed inwardly of the container from the lowest portion of the bottom; a step for heating the domed bottom portion of the secondary article to increase the degree of recess of the thick portion by preferentially shrinking the bottom portion in order to obtain a tertiary article having a bottom portion where the periphery of the thick portion is flattened;

a step for heating the tertiary article inclusive of the bottom portion and the barrel portion thereof in order to obtain a quaternary article of which the barrel portion is chiefly shrunk; and

a step for subjecting the quaternary article that is heated to the secondary blow molding to obtain a final container.

[0022] According to the present invention, furthermore, there is provided a one-piece type heat resistant polyester bottle having excellent strength in the bottom portion, heat resistance, symmetrical panel-sinking stability in the vacuum pressure and self-standing stability obtained by stretch-blow-molding a thermoplastic polyester and having a neck portion, a barrel portion which is drawn and is heat-set and a bottom portion with a recessed central portion, the barrel portion thereof being provided with a panel-rib structure for symmetrical panel-sinking stability in the vacuum pressure, wherein the bottom portion includes a bottom center portion having a thick portion at the center which is inwardly recessed in the axial direction of the container and a peripheral grounding portion which downwardly extends in the axial direction beyond the bottom center portion, the portions excluding neck portion, part of the barrel portion continuous to the neck portion and thick portion at the center of the bottom portion, have a thickness which is drawn to not larger than 0.6 mm and are molecularly oriented to have birefringence in (the circumferential direction - the thickness direction) of not smaller than 0.070 and are further heat-set to have a crystallinity of not smaller than 35%, and the inner side and the outer side of the barrel panel portion have nearly the same crystallinity, or the inner side has a crystallinity which is larger than that of the outer side.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023]

Fig. 1 is a side view illustrating a preformed article used in the present invention;

Fig. 2 is a diagram illustrating a step of molding according to a first embodiment of the present invention;

Fig. 3 is a diagram illustrating a step of molding according to a second embodiment of the present invention;

Fig. 4 is a diagram for explaining a method of pushing the bottom portion of a secondary article according to the second embodiment of the present invention;

Fig. 5 is a diagram illustrating the whole arrangement of a production apparatus with which the method of the present invention is put into practice;

Fig. 6 is a diagram illustrating a step of primary blow molding according to the first embodiment of the present invention;

Fig. 7 is a diagram illustrating a step of molding according to the second embodiment of the present invention;

Fig. 8 is a diagram illustrating, on an enlarged scale, the shape of bottom portion of the secondary article obtained through the molding step shown in Fig. 7;

Fig. 9 is a diagram illustrating, on an enlarged scale, the shape of bottom portion of a tertiary article after the bottom portion of the secondary article shown in Fig. 8 is heated;

Fig. 10 is a diagram for explaining the step of molding according to the second embodiment of the present invention;

Fig. 11 is a side view for explaining the structure of a polyester bottle of the present invention; and

Fig. 12 is a bottom view of the bottle of Fig. 12.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The present invention is concerned with a method of producing a heat-resistant container having a bottom portion of a reduced thickness and excellent heat resistance relying upon the two-step blow-molding method and a container produced by this method.

[0025] According to the study conducted by the present inventors, it was found that a bottom portion having favorable heat resistance is obtained when the bottom portion of the container is drawn at a relatively high draw ratio to reduce its thickness and when this portion is heat-set, so that the crystallinity at the bottom portion is increased to be not smaller than, for example, 35%. In producing such a container relying upon the two-stage blow-molding method, it was further found that the thickness of the bottom portion of the secondary article subjected to the primary blow molding must have been reduced.

[0026] The inventors have furthered the study and have learned that the degree of drawing the bottom portion of the secondary article, i.e., the degree of reducing the thickness, greatly affects properties of the container. For example,

when the bottom portion of the secondary article except the central thick portion is drawn to a small degree and has a thickness of not smaller than 0.6 mm, the bottom portion is whitened when it is heated in an attempt to obtain a desired crystallinity by heat-setting. In the bottom portion that is whitened, the degree of crystallization by orientation is small and the crystallinity is raised due chiefly to spherulit creating a relatively brittle state. When the whitened portion exists over a relatively wide area, the shock resistance decreases. Moreover, the whitened portion has poor transparency. Therefore, the whitened portion that exists over a wide area deprives the container of commercial value in regard to its appearance.

[0027] It was found that the crystallinity can be increased to a desirable range without developing whitening when the secondary article is heat-set, the secondary article having a bottom portion of which the thickness is reduced to be not larger than 0.6 mm except the central thick portion by effecting the drawing to a relatively high degree. However, the bottom portion having a reduced thickness as a result of being drawn to a relatively high degree tends to be shrunk in large amounts upon heating, which is a new problem.

[0028] That is, when the secondary article having a bottom portion of a domed shape which is drawn to a high degree to have a reduced thickness is heated for its barrel portion and bottom portion simultaneously, the bottom portion undergoes shrinking to a considerable degree yet maintaining roughly the domed bottom shape. When the secondary article of this state is subjected to the secondary blow molding, the bottom corner portion is drawn excessively and becomes locally very thin to lose the strength. Moreover, the portions which are re-drawn to a large extent lose crystallinity resulting in a decrease in the heat resistance.

[0029] Furthermore, the secondary article having a bottom portion of a shape close to the recessed shape of a final product may be subjected to the primary blow molding with the central portion of bottom of the preform article sandwiched by the stretch rod and the press rod, in order to reduce the thickness of the bottom portion to be not larger than about 0.6 mm. In this case, there remains a portion having a relatively large thickness at the center of the bottom. When such a secondary article is heated at its barrel portion and bottom portion, the recessed portion in the bottom of the secondary article grows extremely and becomes deep. Therefore, the bottom portion shrinks to have a very decreased bottom diameter, so that the final shape after heated becomes considerably different from the shape of bottom of the product. When the article of this state is subjected to the secondary blow molding, the bottom corner portion is drawn to an excess degree and the thickness becomes too small.

[0030] The present inventors have further forwarded the study and have discovered the fact that when a roughly dome-shaped bottom portion of the secondary article having a thickness of not larger than 0.6 mm except the central portion of bottom is, first, heated in a non-contacting manner, the bottom portion shrinks into a shape of a flat plate or a shape which has a recessed portion at the center and a flat periphery yet substantially maintaining the bottom diameter, and that when the tertiary article of which the bottom portion is heat-shrunk is heated for its barrel portion and bottom portion, the barrel portion chiefly undergoes shrinking with the bottom portion roughly maintaining its shape of when it was initially heated, enabling the bottom portion of a quaternary article that is heated to be brought close to the shape of the final product. Moreover, when the quaternary article that is heated at a high temperature is subjected to the secondary blow molding, the bottom portion is redrawn to a low degree to assume a thickness of not larger than 0.6 mm as maintaining high crystallinity except the thick portion at the center of bottom. There is thus obtained a product which is crystallized to a sufficient degree by the heat treatment and has a bottom corner portion that has a suitable thickness and crystallinity.

[0031] In the two-step blow-molding method of the present invention as described above, a article just before being subjected to secondary blow molding, i.e., a quaternary article that has passed through the heat-shrinking step after it was primary blow-molded, is obtained in a form which is as close as possible to the form of the final product that is desired, in order to decrease the redraw ratio in the step of secondary blow molding, to uniformize the thickness of the products and to prevent a drop in the crystallinity. For that, it is important that the bottom portion of the article (quaternary article and tertiary article) before being subjected to the secondary blow molding is formed in a plate-like shape or in a shape in which the central portion of bottom is recessed and the periphery is flattened.

[0032] In order for the quaternary article (or tertiary article) of the present invention to assume such a bottom shape, it is essential that the secondary article obtained by subjecting the preform article to primary blow molding has a domed bottom substantially without undrawn portions (hereinafter referred to as first embodiment) or has a domed bottom with an undrawn thick portion at the center of the bottom, the thick portion being slightly recessed inwardly of the container from the lowest portion of the bottom (hereinafter referred to as second embodiment).

[0033] The domed bottom portion of the secondary article shrinks upon heating substantially like a flat plate. During the heating, however, a thin portion which is quickly heated tends to shrink first. It is therefore desired that the bottom portion of the secondary article has a relatively uniform thickness distribution. The central portion of bottom of the preform article is formed by injection molding to have a thickness which is larger than that of other portions and, hence, the thickness of the secondary article changes depending upon the condition of locking the central portion of bottom at the time of the primary blow molding. According to the first embodiment of the present invention, it is desired that the thickness at the central portion of bottom is not larger than 2 times and, particularly, not larger than 1.5 times the

thickness of other portions of the bottom. According to the second embodiment, furthermore, it is desired that the thick portion at the center of bottom is not smaller than 1.5 times and, particularly, not smaller than 2 times the thickness of other portions of the bottom. When the thickness of central portion of the bottom is small, there results a flat shape upon heating the bottom portion without forming inwardly recessed portion.

[0034] Then, the whole bottom portion of the secondary article is heated at a temperature higher than a shrinking temperature, so that the bottom portion is preferentially shrunk. According to the first embodiment, therefore, there is obtained a tertiary article in which the domed bottom portion is shrunk like a flat plate but the diameter is almost not changed. According to the second embodiment, furthermore, there is obtained a tertiary article in which the central portion of the bottom is recessed to an increased degree and the periphery thereof is flattened without, however, almost permitting the diameter to change.

[0035] Even when the secondary article has a thick portion which is relatively thin at the center of the bottom portion, a recessed portion can be formed at the center of the bottom portion by effecting the heat-shrinking while pushing the thick portion. Deformation of the central portion in the bottom upon pushing proceeds accompanying the shrinking and softening as the bottom portion is heated and, hence, the bottom portion can be recessed and the periphery thereof can be flattened substantially without drawing. Accordingly, the bottom can be recessed with a relatively small pushing force, and the bottom portion only can be processed without affecting the barrel portion of the article.

[0036] The tertiary article having such a bottom shape is processed at a small rate in the secondary blow molding. Accordingly, a desired thickness distribution is maintained in the bottom portion and a drop in the crystallinity is effectively prevented.

[0037] The container obtained by the method of the present invention has a neck portion, a barrel portion that is drawn and is heat-set, and a bottom portion which includes a central portion of bottom having a thick portion at the center and is inwardly recessed in the axial direction of the container and a peripheral grounding portion which downwardly extends in the axial direction beyond the central portion of the bottom.

[0038] The bottom portion of the container has the central portion of bottom and the peripheral grounding portion that extends inwardly in the axial direction from the central portion of bottom, has a uniform thickness even in the bottom corner portions except the central portion of bottom that is inwardly recessed, and is oriented and crystallized by drawing, and is further crystallized to a high degree by heat treatment. Therefore, the bottom portion maintains excellent self-standing stability. Owing to the uniform crystallization, furthermore, the bottom portion exhibits excellent shock resistance. Moreover, the self-standing structure of the bottom portion is prevented from being deformed by heat, and the self-standing stability is excellently maintained even after the bottle is filled with hot content.

[0039] Moreover, the portions, excluding relatively thick portions such as neck portion, part of the barrel portion continuous to the neck portion, and thick portion at the center of the bottom, have a thickness of as small as not larger than 0.6 mm, are molecularly oriented so as to have birefringence represented by a relation (2) described later of not smaller than 0.070 in (the circumferential direction - the thickness direction), and are further crystallized by heat setting so as to have a crystallinity represented by a relation (1) described later of not smaller than 35%.

[0040] Figs. 11 and 12 illustrate a bottle according to the present invention together with thickness sampling positions on the wall of the bottle including a position a near the thick portion at the center of the bottom, a position c at the periphery of the center of the bottom, an intermediate position b thereof, a grounding portion d and an intermediate position e of the barrel portion. These positions serve as sampling positions that will be described later in the embodiments. Reference should be made to Tables 1 and 2 of embodiments described later. In the bottle of the present invention, the thickness is not larger than 0.6 mm even at the position a or the position b which becomes the thickest. Namely, even at the position d which becomes the thinnest, the thickness is reduced to be from 0.5 to 2 times as thick as the thickness at the intermediate position e of the barrel portion. This is quite an astonishing fact. Moreover, Tables 1 and 2 show relationships between the positions on the wall of the bottle and the crystallinity as well as birefringence near the thick portion at the center of the bottom. Even near the thick portion at the center of the bottom which is most likely to remain undrawn, a high degree of orientation has been accomplished exhibiting a birefringence of not smaller than 0.07 like that of the barrel portion. The high degree of molecular orientation near the thick portion at the center of the bottom is due to the fact that the thickness of the portion near the thick portion at the center of the bottom is greatly decreased at the time of stretch-blow molding. By effecting the heat setting in the thus highly molecularly oriented state, crystallization of not smaller than 35% can be imparted even to the vicinity of thick portion at the center of the bottom, the crystallinity being from 0.8 to 1.4 times as great as the crystallinity in the central portion of the barrel portion.

[0041] When the portions excluding relatively thick portions such as neck portion, part of the barrel portion continuous to the neck portion and thick portion at the center of the bottom, are thinner than the above-mentioned range, the bottom portion lacks mechanical strength. When the above-mentioned portions are thicker than the above-mentioned range, the degree of orientation in the bottom becomes insufficient and the shock resistance becomes unsatisfactory. Similarly, when the crystallinity is smaller than 35%, heat resistance becomes insufficient and, particularly, self-standing stability becomes insufficient after the bottle is filled with hot content.

[0042] Furthermore, a structure for symmetrical panel-sinking stability in the vacuum pressure is constituted by a

panel portion and a rib is formed in the uniformly oriented and crystallized barrel portion of the quaternary article in the final step of blow molding and, besides, the heat set is effected relying upon the non-contacting heating system. Thus, the crystallinity of the outer side which tends to increase is decreased, so that the crystallinity becomes nearly the same on the inner side and on the outer side of the barrel panel portion or the crystallinity becomes larger on the inner side. Therefore, the bottle is prevented from being deformed in a deviated manner when it is filled with hot content. When the pressure decreases with a decrease in the temperature, the panel effectively undergoes paneling deformation and the container is effectively prevented from being asymmetrically deformed. This will become obvious from embodiments that will be described later.

Detailed Description of the Preferred Embodiments

[0043] According to the present invention, the preform article heated at a drawing temperature (90 to 110 °C) is subjected to primary blow molding by either a free blow-molding method which effects the blow molding without using the metal mold or a metal mold blow-molding method which effects the blow molding using the metal mold, thereby to obtain a secondary article. At this moment, the thickness of barrel portion and bottom portion of the secondary article is decreased to be substantially not larger than 0.6 mm and, preferably, 0.2 to 0.5 mm except the undrawn portion at the center of the bottom and vicinity of the neck portion, and, then, heating is effected within a short period of time in the step of heat shrinking and heat set. When the thickness of the portion being heated exceeds 0.6 mm, the temperature distribution becomes too great in the direction of thickness by heating in a short period of time and a desirable temperature range cannot be accomplished.

[0044] In producing the secondary article by subjecting the preform article to primary blow molding, it is desired that the drawing ratio in the axial direction is from 2 to 5 times and, particularly, from 2.2 to 4 times and that the drawing ratio in the circumferential direction is from 2.5 to 6.6 times and, particularly, from 3 to 6 times. In the free blow-molding system, the drawing ratios in the axial direction and in the circumferential direction are determined depending upon the shape of the preform article, heating temperature and blow-molding pressure or blow-molding conditions such as drawn form by using a stretch rod, etc.

[0045] Next, the secondary article is subjected to the step of heat set where the bottom portion is preferentially heated to obtain a tertiary article having a bottom portion of a flat shape or of a shape in which the center of the bottom portion is recessed. In this case, it is of course allowable to obtain the central portion of bottom in a recessed shape by the heating while pushing the center of the bottom portion. Then, the bottom portion and the barrel portion are heated to obtain a quaternary article in which chiefly the barrel portion is heat-shrunk in the direction of height and in the direction of diameter. A variety of heating means can be employed such as a heating system using hot air, a solid-contact heating system by successively pushing a heating member in the form of a flat plate from the top of the dome. According to the present invention, however, it is particularly desired to employ an infrared heating system of the non-contact type. With the infrared heating system, part of the infrared-rays transmits into the interior of the plastic material and is absorbed compared with the heating based upon the conduction of heat from the surface by using hot air and, hence, heating is accomplished relatively efficiently. Furthermore, the secondary article may be passed in a revolving manner through a tunnel-like heating member constituted by combining planar infrared radiating members to accomplish the heating within a relatively short period of time of from about 1 to about 15 seconds.

[0046] The temperature at which the secondary article starts shrinking upon heating varies depending upon the drawing conditions of the primary blow molding, temperature at a moment of releasing the internal pressure of the secondary article formed through primary blow molding, etc. Usually, the secondary article starts shrinking at a temperature of from about 60 to about 140 °C. The temperature of the secondary blow molding is usually from 90 to 110 °C or higher, and the secondary article is heated at a shrinking temperature and at a drawing temperature or higher. In the case of the heat-resistant container, it is desired that the barrel portion and bottom portion of the secondary article are finally heated at about 130 to about 220°C, so that it is heat set to have a sufficient crystallinity.

[0047] The quaternary article that is heated shrinks and is crystallized and the residual stress is relaxed. Furthermore, the quaternary article is cooled to some extent before it is subjected to the step of the secondary blow molding, and the temperature difference between the inner surface and the outer surface is relaxed due to the effect of heat conduction in the direction of thickness. Usually, a relaxation time of from about 0.3 to about 3 seconds is provided.

[0048] In the step of secondary blow molding, the quaternary article that is heated is stretch-blow-molded by using a metal mold which includes a bottom portion and a barrel portion while holding the mouth and the neck. It is desired that the secondary blow molding is carried out by using a gas of 15 to 40 kg/cm². For the containers that require heat resistance, it is desired that the temperature of the metal mold is maintained at about 70 to about 130 °C while preventing the article from quickly cooling during the secondary blow molding.

[0049] In the present invention, any plastic material can be used provided it can be stretch-blow-molded and heat-set. Advantageously, however, there can be used a thermoplastic polyester and, particularly, an ethylene terephthalate thermoplastic polyester. It is allowable to use a polycarbonate or an arylate resin as a matter of course.

[0050] As the ethylene terephthalate thermoplastic polyester, there can be used thermoplastic polyester in which ethylene terephthalate units occupy most of, and, generally, not smaller than 70 mol %, and, particularly, not smaller than 80 mol % of the ester recurring units, the thermoplastic polyester having a glass transition point (T_g) of from 50 to 90 °C. and, particularly, from 55 to 80 °C, and a melting point (T_m) of from 200 to 275 °C and, particularly, from 220 to 270 °C.

[0051] Though a homopolyethylene terephthalate is desirable from the standpoint of heat resistance, it is also allowable to use a copolymerized polyester containing small amounts of ester units other than the ethylene terephthalate units.

[0052] Examples of the dibasic acid other than terephthalic acid include aromatic dicarboxylic acid such as isophthalic acid, phthalic acid, naphthalenedicarboxylic acid and the like acid; alicyclic dicarboxylic acid such as cyclohexanedicarboxylic acid and the like acid; and aliphatic dicarboxylic acid such as succinic acid, adipic acid, sebacic acid, dodecanedioic acid and the like acid, which may be used alone or in combination. As the diol components other than ethylene glycol, there can be exemplified propylene glycol, 1,4-butanediol, diethylene glycol, 1,6-hexylene glycol, cyclohexane dimethanol, ethylene oxide adduct of bisphenol A, which may be used in a single kind or in a combination of two more kinds.

[0053] The ethylene terephthalate thermoplastic polyester that is used should have a molecular weight which is large enough for forming, at least, a film, and should be the one of the injection grade or of the extrusion grade depending upon the use. It is desired that the intrinsic viscosity (I.V.) generally lies from 0.6 to 1.4 dl/g and, particularly, from 0.63 to 1.3 dl/g.

[0054] The plastic material is molded into a preform article by injection molding. That is, the plastic material is melt-injected into an injection mold that is cooled, and is cooled to obtain an amorphous preform article of the plastic material.

[0055] Fig. 1 illustrates an example of the preform article. The preform article 1 comprises a neck portion 2, a barrel portion 3 and a closed bottom portion 4, and the neck portion 2 is provided with a closure-fastening mechanism 5 such as screw and a support ring 6 for holding the container.

[0056] Any widely known injection machine can be used which is equipped with an injection plunger or a screw, and the mixture is injected into the injection mold through nozzle, sprue and gate. Then, the polyester and the like flow into the cavity of the injection mold where they are solidified into a preform article for stretch-blow molding.

[0057] There is used an injection mold having a cavity that corresponds to the shape of the container, and it is desired to use an injector of the one-gate type or the multi-gate type. It is desired that the temperature of injection is from 270 to 310 °C and the pressure is from about 28 to about 110 kg/cm².

[0058] In order to enhance the heat resistance and rigidity at the mouth of the bottle, furthermore, it is desired to crystallize and whiten the mouth of the preform article by heating in advance. Crystallization of the mouth portion by heating is effected by heating the mouth portion of the preform article at a temperature of generally from 140 to 220 °C and, particularly, at 160 to 210 °C in a state where the mouth portion is thermally insulated from other portions. It is desired that the crystallinity at the mouth portion of the preform article is not lower than 25%.

[0059] The bottom portion of the preform article can similarly be crystallized by heating over a range of a diameter of about 8 mm in advance. This makes it possible to enhance the heat resistance and rigidity at that portion and to prevent amorphous undrawn portion and lowly drawn portion from remaining near the center of the bottom at the time of stretch-blow molding. When the preform article is blow-molded being sandwiched between the stretch rod and the press rod, furthermore, the portion that is held is the central portion of the bottom. It is therefore desired that this portion is whitened by being crystallized.

[0060] The invention will now be described in detail with reference to the accompanying drawings.

[0061] Fig. 2 illustrates steps for producing a heat-resistant container according to a first embodiment of the present invention, wherein a preform article 11 (Fig. 2(A)) obtained by injection molding or the like is heated at a drawing temperature (90 to 110 °C) and is biaxially stretch-blow-molded by free blowing to obtain a secondary article 12 (Fig. 2(B)) having a domed bottom. Usually, the thick portion at the center of the domed bottom of the secondary article 12 that is obtained has been substantially drawn and has a thickness of not larger than two times as large as the thickness of other portions of the bottom.

[0062] The whole bottom portion of the secondary article 12 is heated at a temperature higher than the shrinking temperature, so that it is shrunk. The domed bottom portion has been blown to a sufficient degree at the time of the primary blow molding except the central portion and the vicinity thereof, and shrinks like a flat plate upon heating in a manner that the surface area decreases. At this moment, the diameter of the bottom portion almost does not change. Heat-shrinking of the bottom portion starts with the center of the bottom and then successively spreads in the direction of diameter.

[0063] To obtain the bottom portion of the secondary article in a flat shape by heating, it is important that the thickness of thick portion at the center of bottom of the secondary article 12 is relatively small as described above. It is desired that the thickness of thick portion at the center of bottom is not larger than two times and, particularly, not larger than 1.5 times as large as the thickness of other portions of the bottom. When the thickness of thick portion at the center

[0099] To measure the retardation, the sample was sliced by using a microtome (manufactured by Reichert-Jung) maintaining a thickness of 10 μm such that the cross section was in the circumferential direction and in the thickness direction of the bottle.

5 (IV) Falling test.

[0100] A bottle was filled with the water up to 40 mm below the end of mouth of the bottle. The bottle filled with the water was allowed to fall vertically onto a concrete floor five times at room temperature from a height of 1.2 m. When the bottle was cracked before five times, the vertical fall up to that number of times was recorded. The bottles produced under the same conditions were tested with $n = 3$.

(V) Heat resistance test.

[0101] A mark was attached at a height of 30 mm above the bottom portion of the bottle, and water was introduced up to the mark to measure the volume V_0 . The water was then drained and the water heated at 85 °C was introduced up to 40 mm below the end of the mouth of the bottle. After fitted with the cap, the bottle was left to stand in a lying state for one minute, and then in an erected state for four minutes. After being cooled with water of a normal temperature, the water contained therein was drained. Then, the water was introduced again up to the marked position to measure the volume V_1 . By using these values, a volume shrinking factor $V' = (V_0 - V_1)/V_0 \times 100$ (%) in the bottom portion and in the vicinity thereof was calculated.

(Example 1)

[0102] A preform article having bottom weighing 49 g was obtained by injection-molding a polyethylene terephthalate resin (J125TKL having an intrinsic viscosity of 0.78 dl/g and a DEG copolymerization degree of 1.3% by weight, manufactured by Mitsui PET Resin Co.). The mouth portion and an area of a radius of not larger than 8 mm at the center of the bottom were heat-treated and crystallized so as to be whitened. The preform article was heated by an infrared heater and was subjected to stretch-blow molding while being sandwiched between a stretch rod and a press rod using a metal mold for primary blow molding (having bottom shape of bottle corresponding to that of Fig. 8). The article was then passed in a revolving manner through a tunnel-like infrared heating member so as to be heat-shrunk, and was then subjected to stretch-blow molding using a metal mold (metal mold for secondary blow molding heated at 70 °C) equipped with a cavity corresponding to Figs. 11 and 12, to obtain a self-standing one-piece bottle having a content of about 1.5 liters (Fig. 11). The temperature of the preform article was measured at a central position in the direction of height and the temperature for heating the bottle was measured at a central portion of the barrel and at a peripheral portion of bottom of the bottle when it has come out from the tunnel-like heating member but just before the metal mold is closed by using an infrared radiation thermometer. By changing these temperatures, there were obtained bottles A and B. The tunnel-like infrared heating member was controlled to heat the bottom portion first and to heat the bottom and the barrel next in bottle A. But it was controlled to heat the bottom and the barrel simultaneously in bottle B.

40 (Example 2)

[0103] A preform article was obtained in the same manner as in Example 1, and the mouth portion only was crystallized. The preform article was then heated by using an infrared heater and was subjected to draw-blow molding (free blow molding) by using a stretch in a state where the mouth portion only was secured but the outer periphery and the bottom portion were not locked. The article was then inserted in a cylindrical infrared heating member and was heat-shrunk, and was then subjected to stretch-blow molding using the metal mold for secondary blow molding of Example 1 to obtain a bottle having a shape shown in Fig. 11. By changing the molding temperature, there were obtained bottles C and D.

50 (Comparative Example 1)

[0104] A preform article weighing 59 g was obtained and was heated in the same manner as in Example 1. Next, the preform article was subjected to stretch-blow molding using a metal mold for blow molding and a stretch rod to prepare a bottle the same as the one shown in Fig. 11. Bottle E was obtained by using a metal mold heated at 140 °C at the barrel portion and at 70 °C at the bottom portion, and a bottle F was obtained by using a metal mold heated at 160 °C both at the barrel portion and the bottom portion.

[0105] In the bottom portions of these bottles, the positions separated away from the center of the bottom by 5 mm, 15 mm, 25 mm and 35 mm were denoted as a, b, c and d. As for the barrel portion of the bottle, the central portion in

the direction of height (position 0 mm away from the end of the mouth) was denoted as e, the central portion of the panel was denoted as f (Fig. 11), and thicknesses and crystallinities of these portions were measured. As for the portion f, the sample was divided into an inner half and an outer half to take measurement. The results were as shown in Table 1. As for the bottles A and B, however, the portion a was an undrawn, whitened and crystallized portion (thick portion at the center) which was not covered in the scope of claim of the present application, and was not measured. The birefringence An was measured at the portion b for the bottles A and B, and was measured at the portion a for other bottles. Since the birefringence may vary in the direction of thickness, it was measured nearly at the center of the thickness.

[0106] The falling test was carried out with $n = 3$. An open circle ○ represents the case of when none of the three bottles was cracked, Δ represents the case of when two of them were not cracked, and X represents the case of when two or more of them were cracked. The results were as shown in Table 2.

[0107] Table 2 also shows the results of heat resistance testing, thickness ratio of the bottom portion and the central portion of barrel, as well as crystallinity ratios calculated from Table 1.

[0108] As will be obvious from Tables 1 and 2, the one-piece type heat resistant polyester bottles covered by the scope of claim of the present application were bottles A, C and D. These bottles possessed a thickness of not larger than 0.6 mm in the bottom portion except the thick central portion of bottom and in the center of the barrel, possessed a birefringence in (the circumferential direction - the thickness direction) of not smaller than 0.070, and exhibited a crystallinity of not smaller than 35%, thus being drawn to a sufficient degree. Therefore, a high strength and a high heat resistance could be expected. In the falling test in practice, the bottles were not cracked at all and exhibited a small volume shrinking factor in the heat resistance testing.

[0109] In the case of the bottle B, the portion b was not thinner than 0.6 mm and was drawn little and was heated at a temperature which was lowered by the amount of thickness (the smaller the thickness, the higher the temperature as heated by the infrared heating member) and, hence, exhibited a small crystallinity and a small birefringence. The portion d exhibited a crystallinity of as small as 27.1%. The temperature at the bottom portion was 145 °C as measured by the infrared radiation thermometer, from which it was difficult to consider that the bottom portion was heated at a temperature which was very much lower than 145 °C though the measuring position was slightly different. Therefore, the bottle was taken out just before it was subjected to the secondary blow molding, i.e., after it was heat-shrunk in order to measure the crystallinity and thickness of a portion corresponding to the bottom portion d to be 39.5% and 515 μm. It was therefore considered that the portion d was redrawn at a very large rate through the secondary blow molding and has lost crystallinity to a great degree. The fact that the crystallinity has changed to a large degree means that the polymer structure has changed. In this case, the thickness was reduced from 515 μm to 102 μm, and the shape of bottom of the bottle after heated became considerably different from the shape of bottom of the final bottle shown in Fig. 11 because of a considerably large processing rate. Therefore, though processed under high temperature conditions, it is considered that the bottom portion was severely drawn destroying the polymer structure through the heating and leaving residual strain. Because of these reasons, bottle B possessed poor heat resistance and cracked at an extremely thin portion when it was dropped. In the heat resistance testing, the bottles E and F exhibited large volume shrinking factors V' at the bottom portion and in the vicinity thereof. In the case of the bottle E, the central portion of bottom was drawn to a small degree and was not crystallized. Besides, the metal mold was heated at a temperature of as low as 70 °C at the bottom portion thereof. It is therefore considered that the bottom portion was not heat-set and exhibited a large volume shrinking factor through the heat resistance testing. In the case of the bottle F, the bottom portion was more drawn than that of the bottle E but was still considerably thick and was drawn to a small degree. Besides, the bottle F was thinly whitened. This was presumably because the metal mold was heated at a temperature of as high as 160 °C and spherulite crystals have grown in the lowly-stretch portions due to crystallization by heating. Therefore, the resistance against the falling impact was poor.

[0110] The panel portions of the bottles A, B, C and D exhibited crystallinities that were larger on the inner side than on the outer side. On the other hand, the panel portions of the bottles E and F exhibited crystallinities that were smaller on the inner side than on the outer side. 100 Bottles were subjected to the heat resistance testing (V) that was mentioned above. The bottles A, B, C, D, E and F developed asymmetrical deformation of the panels at frequencies of 0/100, 0/100, 0/100, 18/100 and 7/100.

Table 1

Temp. of perform (°C)	Temp. of heating bottle (°C)	Bottom (°C)	Barrel (°C)	Thickness (μm)					Crystallinity (%)						
				a	b	c	d	e	a	b	c	d	e	f	
A	107	174	150	-	469	359	240	322	-	43.2	42.6	41.1	38.8	38.2	39.1
B	104	145	140	-	628	302	102	365	-	32.5	38.6	27.1	36.4	36.1	36.9
C	105	192	200	460	402	305	286	420	49.7	46.6	44.3	42.5	52.1	51.7	52.6
D	100	180	172	442	431	385	330	431	46.5	44.9	41.3	37.6	44.3	42.3	43.3
E	107	-	-	3010	3270	1730	387	320	0	0	7.7	28.1	35.7	36.0	35.3
F	102	-	-	1980	1100	1380	420	380	17.1	22.7	17.9	24	40.8	41.5	40.

out-
in-
side
side

Table 2

	Thickness of bottom/ thickness of central portion of barrel				crystallinity of bottom/ crystallinity of central portion of barrel				Biref- ringence Δn	Falling test	Heat-resistance test	Vol. shrinking factor: $V (\%)$
	a	b	c	d	a	b	c	d				
A	-	1.46	1.11	0.75	-	1.11	1.10	1.06	0.093	O		0.94
B	-	1.72	0.83	0.28	-	0.89	1.06	0.74	0.0494	Δ		6.2
C	1.10	0.96	0.73	0.68	0.95	0.89	0.85	0.82	0.121	O		0.68
D	1.03	1.00	0.89	0.77	1.05	1.01	0.93	0.85	0.103	O		1.1
E	9.41	10.22	5.41	1.21	0	0	0.22	0.79	0.005	Δ		4.2
F	5.21	2.89	3.63	1.11	0.42	0.56	0.44	0.59	0.019	X		3.0

O: good, Δ : fair, X: bad

(Example 3)

[0111] By using an apparatus of Fig. 5, a heat-resistant polyethylene terephthalate (PET) bottle shown in Fig. 11 which is a finally formed article was prepared having an outer diameter of 94 mm, an overall height of 305 mm (height of heating portion of 280 mm), a capacity of 1500 ml and a recessed bottom portion.

[0112] A predetermined preform article was heated at 100 °C, and was subjected to primary blow molding using a metal mold as shown in Fig. 7(A) maintained at 70 °C to obtain a secondary article having a recessed portion of 3 mm deep at the center of the bottom portion and a domed bottom portion of a relatively uniform thickness. The secondary article was allowed to pass in a revolving manner over a period of eight seconds through a tunnel-like infrared heating member which was divided into three zones along the circumference to possess surface temperatures of from 500 to 700 °C, in order to obtain a quaternary article having a bottom portion which was shrunk nearly flatly, having a barrel portion which was shrunk in the direction of height and in the direction of diameter, and being finally heated at the barrel portion and at the bottom portion both at a temperature of about 180 °C. The quaternary article was subjected to secondary blow molding to obtain a final product. The final product was filled with the hot water heated at 95 °C and was evaluated for its heat resistance (favorable range: change of volume is not larger than 2%) relying upon a change in the volume. Favorable results were obtained.

Claims

1. A method of producing a biaxially-stretch-blow-molded container by blow-molding a cylindrical preform article (1,11) with bottom that is heated at a drawing temperature, comprising:
 - i) subjecting the preform article (11) to primary blow molding to obtain a biaxially drawn secondary article (12) having a domed bottom portion without substantially containing undrawn portions;
 - ii) heating the domed bottom portion of the secondary article to preferentially shrink the bottom portion in order to obtain a tertiary article (14) having a flat bottom portion;
 - iii) heating the tertiary article (14) inclusive of the bottom portion and the barrel portion thereof in order to obtain a quaternary article (16) of which the barrel portion is chiefly shrunk; and
 - iv) subjecting the heated quaternary article (16) to secondary blow molding to obtain a final container (18).
2. A method of producing a biaxially-stretch-blow-molded container by blow-molded a cylindrical preform article (1,11) with bottom that is heated at a drawing temperature, comprising:
 - i) subjecting the preform article (11) to primary blow molding to obtain a biaxially drawn secondary article (12) having a domed bottom portion (21) with an undrawn thick portion (22) at the center of the bottom, the thick portion being slightly recessed inwardly of the container from the lowest portion of the bottom;
 - ii) heating the domed bottom portion (21) of the secondary article (12) to increase the degree of recess of the thick portion (22) by preferentially shrinking the bottom portion in order to obtain a tertiary article (24) having a bottom portion where the periphery of the thick portion is flattened;
 - iii) heating the tertiary article (24) inclusive of the bottom portion and the barrel portion thereof in order to obtain a quaternary article (16) of which the barrel portion is chiefly shrunk; and
 - iv) subjecting the heated quaternary article (16) to secondary blow molding to obtain a final container (18).
3. A method of producing a biaxially-stretch-blow-molded container as claimed in Claim 2, wherein in step ii) the domed bottom portion (21) of the secondary article (12) is heated and is preferentially shrunk while pushing the thick portion (22) at the center of the bottom of the secondary article (12) in order to increase the degree of recess of the thick portion (22), thereby to obtain the tertiary article (24) having a bottom portion where the periphery of the thick portion (22) is flattened.
4. A method of producing a biaxially-stretch-blow-molded container as claimed in any one of Claims 1 to 3, wherein the drawing in the primary blow molding is effected under the conditions where at least the outer periphery and the bottom portion of the preform article are not locked.
5. A one-piece type heat resistant polyester bottle (61) having excellent strength in the bottom portion, heat resistance, symmetrical panel-sinking stability in the vacuum pressure and self-standing stability obtained by stretch-blow-molding a thermoplastic polyester and having a neck portion (62), a barrel portion (63,64) which is drawn and is heat-set and a bottom portion (65) with a recessed central portion (72), the barrel portion (64) thereof being provided

with a panel-rib structure (71) to prevent poor-looking deformation of the bottle caused by the vacuum pressure, wherein the bottom portion (65) includes a bottom center portion having a thick portion at the center which is inwardly recessed in the axial direction of the container and a peripheral grounding portion (73) which downwardly extends in the axial direction beyond the bottom center portion (65), the portions excluding neck portion, part of the barrel portion continuous to the neck portion and thick portion at the center of the bottom portion, have a thickness which is reduced to smaller than 0.8 mm and are molecularly oriented to have a birefringence in (the circumferential direction - the thickness direction) of not smaller than 0.070 and are further heat-set to have a crystallinity of not smaller than 35%, and the inner side and the outer side of the barrel panel portion have nearly the same crystallinity, or the inner side has a crystallinity which is larger than that of the outer side.

Patentansprüche

1. Verfahren zum Herstellen eines biaxial streckgeblasenen Behälters durch Blasformen eines zylindrischen Vorform-Gegenstands (1, 11) mit einem Boden, der auf eine Ziehtemperatur erhitzt wird, mit folgenden Stufen:
 - i) Primäres Blasformen des Vorform-Gegenstands (11), um einen biaxial gezogenen sekundären Gegenstand (12) zu erhalten, der einen konvex gewölbten Bodenabschnitt aufweist, welcher im wesentlichen keine ungezogenen Bereiche enthält;
 - ii) Erhitzen des konvex gewölbten Bodenabschnitts des sekundären Gegenstands, um vorzugsweise den Bodenabschnitt zu schrumpfen, um einen tertiären Gegenstand (14) mit einem flachen Bodenabschnitt zu erhalten wird,
 - iii) Erhitzen des tertiären Gegenstands (14) einschließlich seines Bodenabschnitts und seines Zylinderabschnitts, um einen quaternären Gegenstand (16) zu erhalten, dessen Zylinderabschnitt im wesentlichen geschrumpft ist, und
 - iv) sekundäres Blasformen des erhitzten quaternären Gegenstand (16), um den endgültigen Behälter (18) zu erhalten.
2. Verfahren zum Herstellen eines biaxial streckgeblasenen Behälters durch Blasformen eines zylindrischen Vorform-Gegenstands (1, 11) mit einem Boden, der auf eine Ziehtemperatur erhitzt wird, mit folgenden Stufen:
 - i) Primäres Blasformen eines Vorform-Gegenstands (11), um einen biaxial gezogenen sekundären Gegenstand (12) zu erhalten, der einen konvex gewölbten Bodenabschnitt (21) mit einem dicken ungezogenen Bereich (22) in der Bodenmitte aufweist, wobei der dicke Bereich vom untersten Bodenabschnitt zum Inneren des Behälters hin eine leichte Vertiefung aufweist,
 - ii) Erhitzen des konvex gewölbten Bodenabschnitts (21) des sekundären Gegenstands (12), um das Ausmaß der Vertiefung des dicken Bereichs (22) durch vorzugsweise Schrumpfen des Bodenabschnitts zu vergrößern, um einen tertiären Gegenstand (24) mit einem Bodenabschnitt zu erhalten, in dem der Umfang des dicken Bereichs abgeflacht ist,
 - iii) Erhitzen des tertiären Gegenstands (24) einschließlich seines Bodenabschnitts und seines Zylinderabschnitts, um einen quaternären Gegenstand (16) zu erhalten, dessen Zylinderabschnitt im wesentlichen geschrumpft ist, und
 - iv) sekundäres Blasformen des erhitzten quaternären Gegenstands (16), um einen endgültigen Behälter (18) zu erhalten.
3. Verfahren zum Herstellen eines biaxial streckgeblasenen Behälters nach Anspruch 2, worin in der Stufe ii) der konvex gewölbte Bodenabschnitt (21) des sekundären Gegenstands (12) erhitzt und vorzugsweise geschrumpft wird, während der dicke Bereich (22) in der Mitte des Bodens des sekundären Gegenstands (12) gedrückt wird, um das Ausmaß der Vertiefung des dicken Bereichs (22) zu erhöhen und dadurch den tertiären Gegenstand (24) mit einem Bodenabschnitt zu erhalten, in dem der Umfang des dicken Bereichs (22) abgeflacht ist.
4. Verfahren zum Herstellen eines biaxial streckgeblasenen Behälters nach einem der Ansprüche 1 bis 3, worin das

Ziehen beim primären Blasformen unter Bedingungen stattfindet, bei denen mindestens ein Teil des Außenumfang und der Bodenabschnitt des Vorform-Gegenstands nicht festgehalten werden.

- 5 5. Einstückige wärmebeständige Polyesterflasche (61) mit einer hervorragenden Festigkeit im Bodenabschnitt, mit Wärmebeständigkeit, mit symmetrischer Platteneinsenkstabilität unter Vakuumdruck und mit Selbststehstabilität, die durch Streckblasen eines thermoplastischen Polyesters erhalten worden ist und einen Halsabschnitt (62), einen Zylinderabschnitt (63, 64), der gezogen und wärmegehärtet ist, und einen Bodenabschnitt (65) mit einer Vertiefung im Mittelbereich (72) aufweist, wobei der Zylinderabschnitt (64) der Flasche mit einer Plattenrippenstruktur (70, 71) versehen ist, um eine durch den Vakuumdruck verursachte, schlecht aussehende Verformung der Flasche zu vermeiden, wobei der Bodenabschnitt (65) einen Bodenmittelbereich mit einem dicken Abschnitt in der Mitte aufweist, der in axialer Richtung des Behälters mit einer Vertiefung nach Innen versehen ist, und einen Umfangsbodenabschnitt (73) aufweist, der sich in axialer Richtung nach unten über den Bodenmittelabschnitt (65) hinausstreckt, wobei die Abschnitte, ausgenommen den Halsabschnitt und den Teil des Zylinderabschnitts, der kontinuierlich in den Halsabschnitt übergeht, sowie der dicke Bereich in der Mitte des Bodenabschnitts eine Dicke aufweisen, die auf weniger als 0,8 mm vermindert ist, und molekular orientiert sind, so dass sie eine Doppelbrechung (in der Umfangsrichtung - der Dickenrichtung) von nicht weniger als 0,070 aufweisen und ferner wärmegehärtet sind, um eine Kristallinität von nicht weniger als 35% zu erhalten, wobei auf der Innenseite und der Außenseite des Zylinderplattenabschnitts etwa die gleiche Kristallinität vorliegt oder die Kristallinität der Innenseite größer ist als jene der Außenseite.

Revendications

- 25 1. Procédé de production d'un récipient moulé par soufflage étiré biaxialement, par moulage par soufflage d'un article de préforme cylindrique (1, 11) ayant un fond qui est chauffé à une température d'étirage, consistant à :
 - i) soumettre l'article de préforme (11) à un moulage par soufflage primaire pour obtenir un article secondaire étiré biaxialement (12) ayant un fond bombé et ne contenant sensiblement pas de parties non étirées ;
 - 30 ii) chauffer le fond bombé de l'article secondaire pour rétracter préférentiellement le fond afin d'obtenir un article tertiaire (14) ayant un fond plat ;
 - iii) chauffer l'article tertiaire (14), y compris son fond et son corps, afin d'obtenir un article quaternaire (16) dont le corps est principalement rétracté ; et
 - iv) soumettre l'article quaternaire chauffé (16) à un moulage par soufflage secondaire pour obtenir un récipient final (18).
- 35 2. Procédé de production d'un récipient moulé par soufflage étiré biaxialement, par moulage par soufflage d'un article de préforme cylindrique (1, 11) ayant un fond qui est chauffé à une température d'étirage, consistant à :
 - i) soumettre l'article de préforme (11) à un moulage par soufflage primaire pour obtenir un article secondaire étiré biaxialement (12) ayant un fond bombé (21) avec une partie épaisse non étirée (22) au centre du fond, la partie épaisse étant légèrement en retrait vers l'intérieur du récipient par rapport à la partie la plus basse du fond ;
 - 40 ii) chauffer le fond bombé (21) de l'article secondaire (12) pour augmenter le degré de retrait de la partie épaisse (22) en rétractant préférentiellement le fond afin d'obtenir un article tertiaire (24) ayant un fond dans lequel la périphérie de la partie épaisse est aplatie ;
 - 45 iii) chauffer l'article tertiaire (24), y compris son fond et son corps, afin d'obtenir un article quaternaire (16) dont le corps est principalement rétracté ; et
 - iv) soumettre l'article quaternaire chauffé (16) à un moulage par soufflage secondaire pour obtenir un récipient final (18).
- 50 3. Procédé de production d'un récipient moulé par soufflage étiré biaxialement selon la revendication 2, dans lequel, dans l'étape ii), le fond bombé (21) de l'article secondaire (12) est chauffé et est préférentiellement rétracté tandis que la partie épaisse (22) au centre du fond de l'article secondaire (12) est poussée afin d'augmenter le degré de retrait de la partie épaisse (22), pour obtenir ainsi l'article tertiaire (24) ayant un fond dans lequel la périphérie de la partie épaisse (22) est aplatie.
- 55 4. Procédé de production d'un récipient moulé par soufflage étiré biaxialement selon l'une quelconque des revendications 1 à 3, dans lequel l'étirage est effectué dans le moulage par soufflage primaire dans les conditions où au

moins la périphérie extérieure et le fond de l'article de préforme ne sont pas bloqués.

5. Flacon en polyester résistant à la chaleur en une seule pièce (61) dont la résistance mécanique du fond, la résistance à la chaleur, la stabilité d'enfoncement de panneau symétrique sous dépression et la stabilité autonome en station debout sont excellentes, obtenu par moulage par soufflage-étirage d'un polyester thermoplastique et ayant un goulot (62), un corps (63, 64) qui est étiré et stabilisé à chaud, et un fond (65) ayant une partie centrale en retrait (72), son corps (64) comportant une structure de nervures-panneaux (70, 71) pour empêcher une déformation inesthétique du flacon provoquée par la dépression, dans lequel le fond (65) comprend une région centrale de fond ayant une partie épaisse au centre qui est en retrait vers l'intérieur dans la direction axiale du récipient et une région de base périphérique (73) qui s'étend vers le bas dans la direction axiale au-delà de la région centrale de fond (65), les différentes parties, à l'exclusion du col, de la région du corps contiguë au col et de la partie épaisse au centre du fond, ont une épaisseur qui est réduite à moins de 0,8 mm et sont orientées moléculairement pour avoir une biréfringence dans (la direction circonférentielle - la direction de l'épaisseur) non inférieure à 0,070 et sont encore stabilisées à chaud pour avoir une cristallinité non inférieure à 35 %, et la face interne et la face externe des panneaux de corps ont presque la même cristallinité, ou bien la face interne a une cristallinité qui est supérieure à celle de la face externe.

FIG. 1

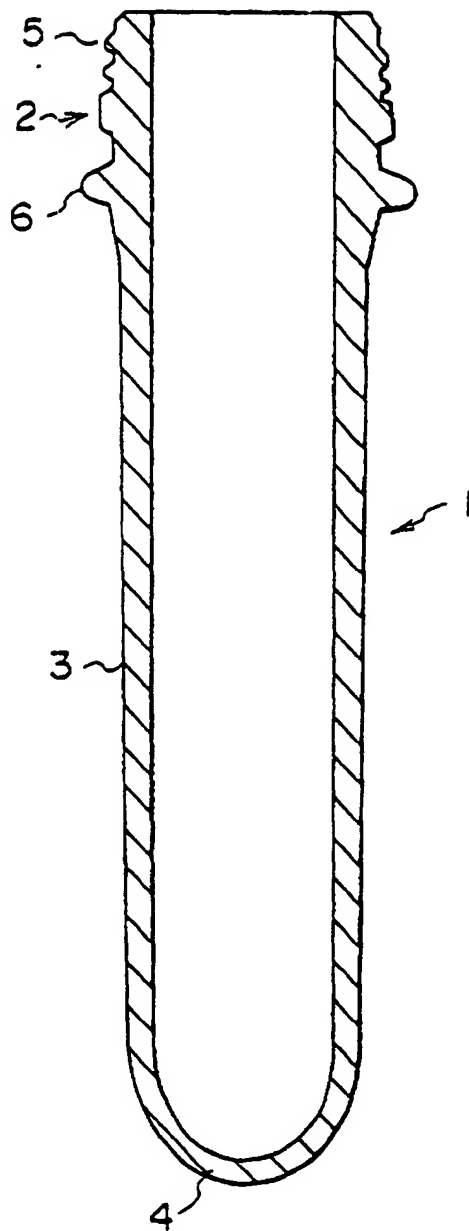


FIG. 2A

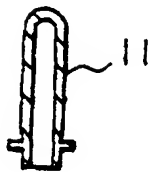


FIG. 2B

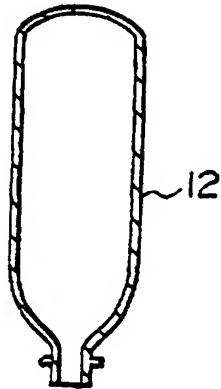


FIG. 2C

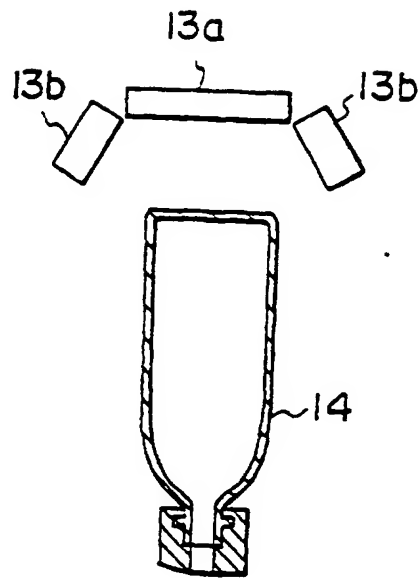


FIG. 2D

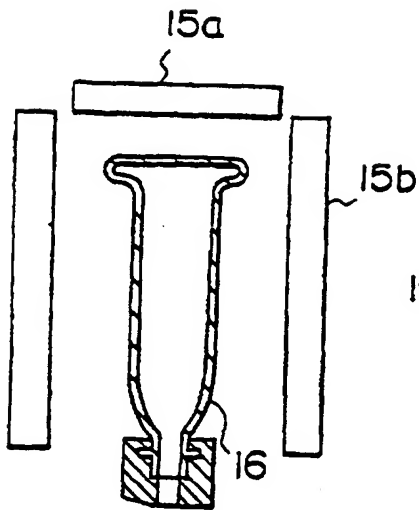


FIG. 2E

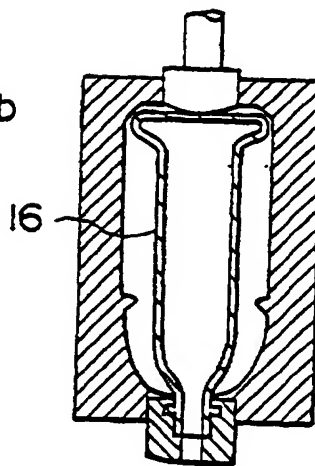


FIG. 2F

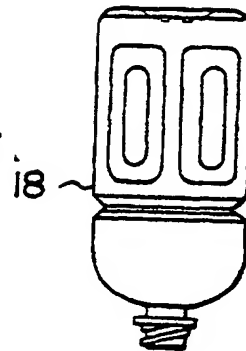


FIG. 3A

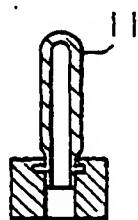


FIG. 3B

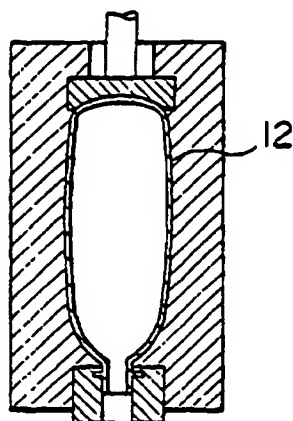


FIG. 3C

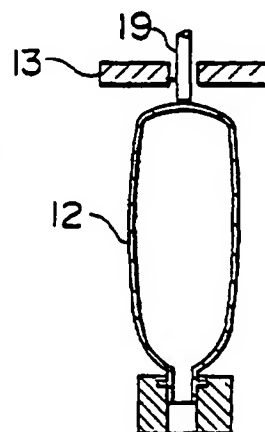


FIG. 3D

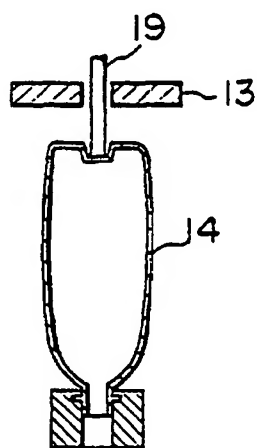


FIG. 3E

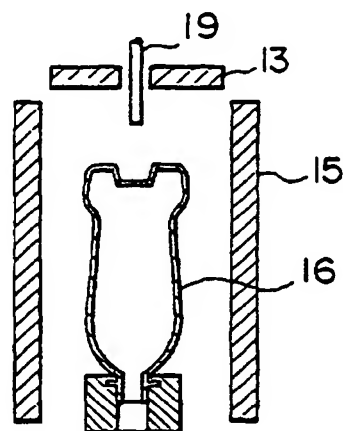


FIG. 3F

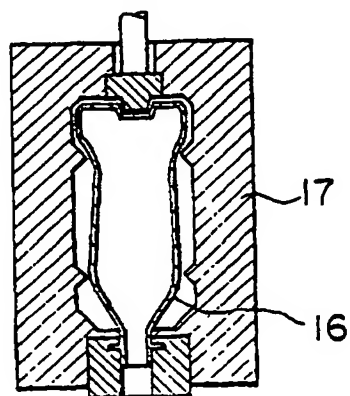


FIG. 3G

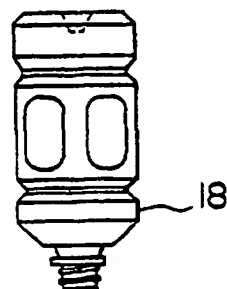


FIG. 4A

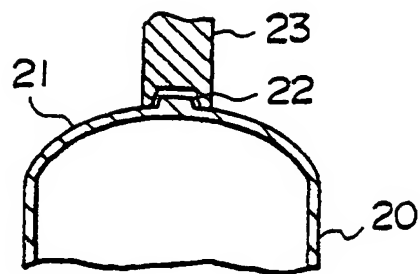


FIG. 4B

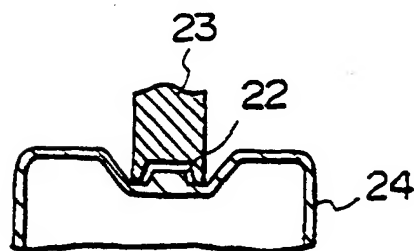


FIG. 5

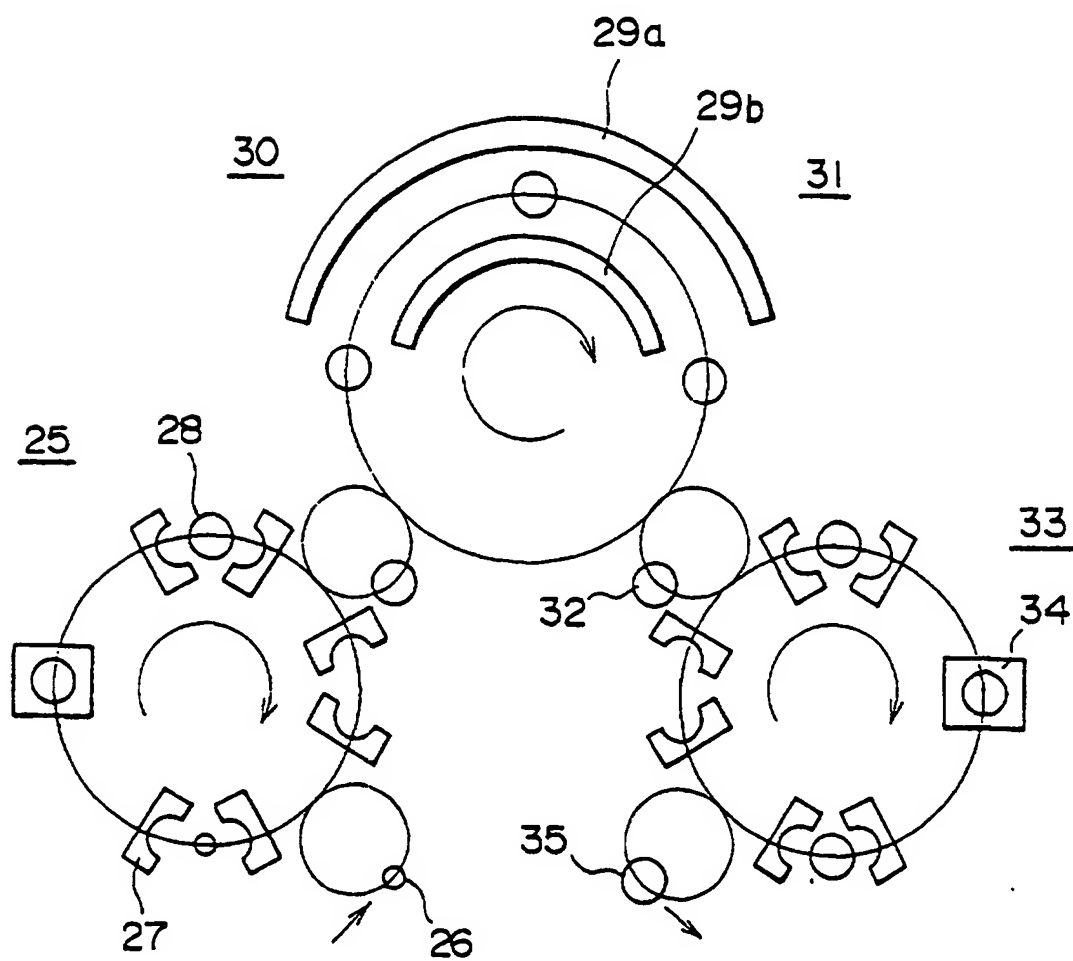


FIG. 6

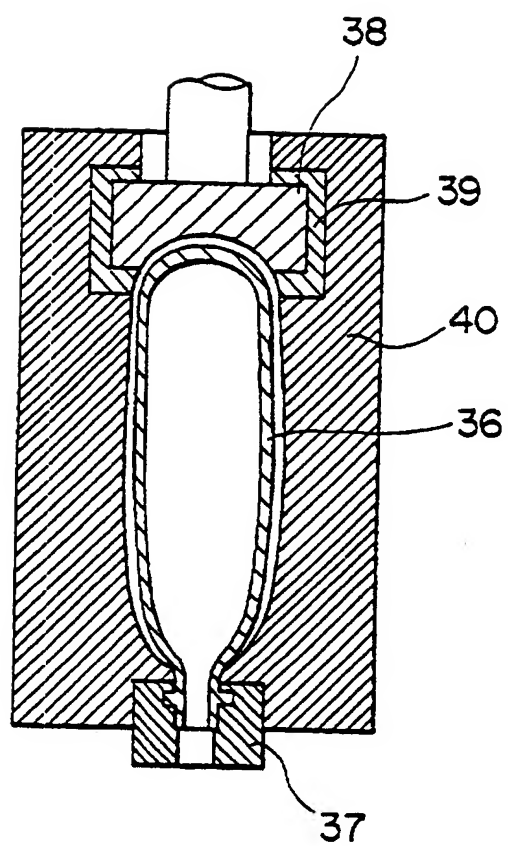


FIG. 7A

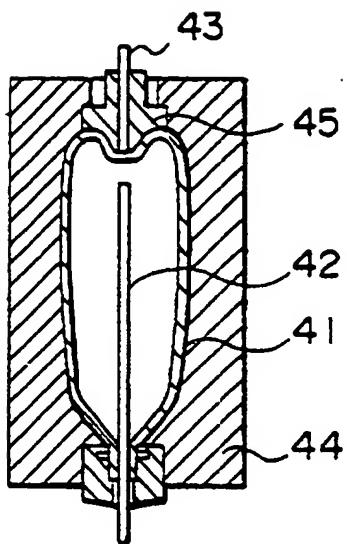


FIG. 7B

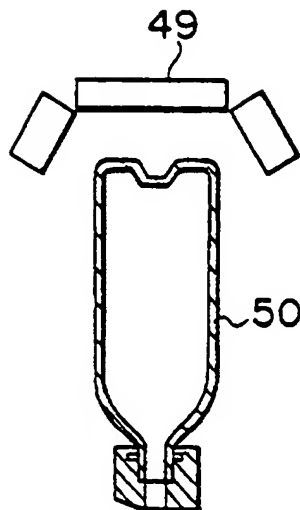


FIG. 7C

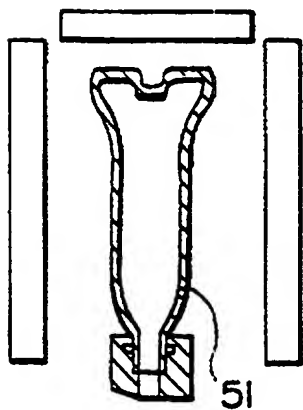


FIG. 7D

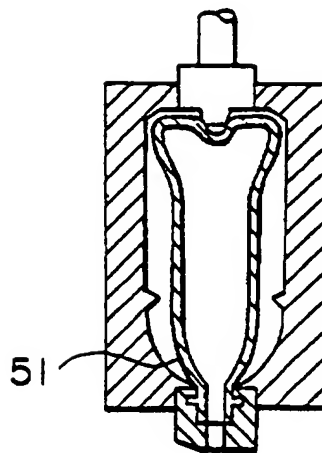


FIG. 8

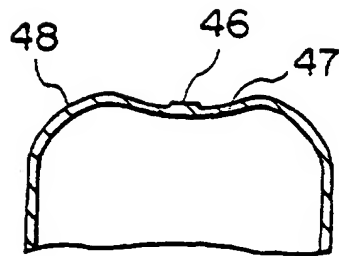


FIG. 9

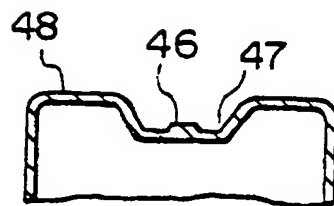


FIG. 10A

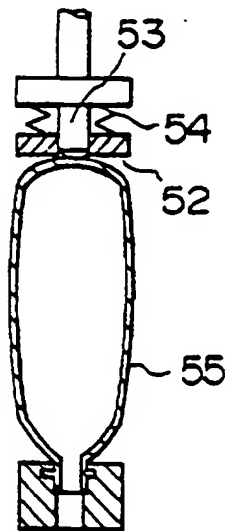


FIG. 10B

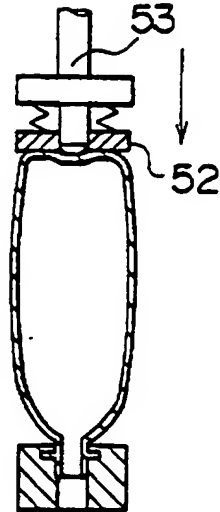


FIG. 10C

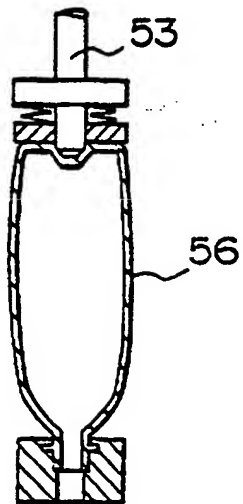


FIG. 10D

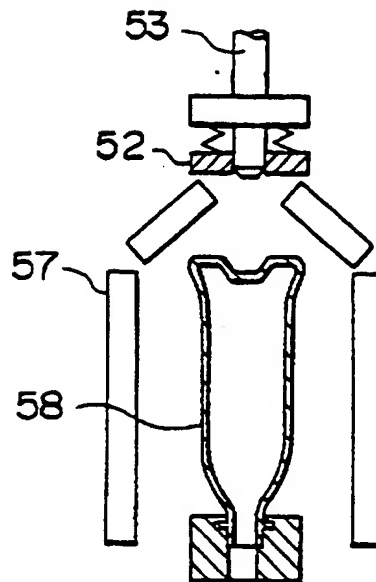


FIG. 11

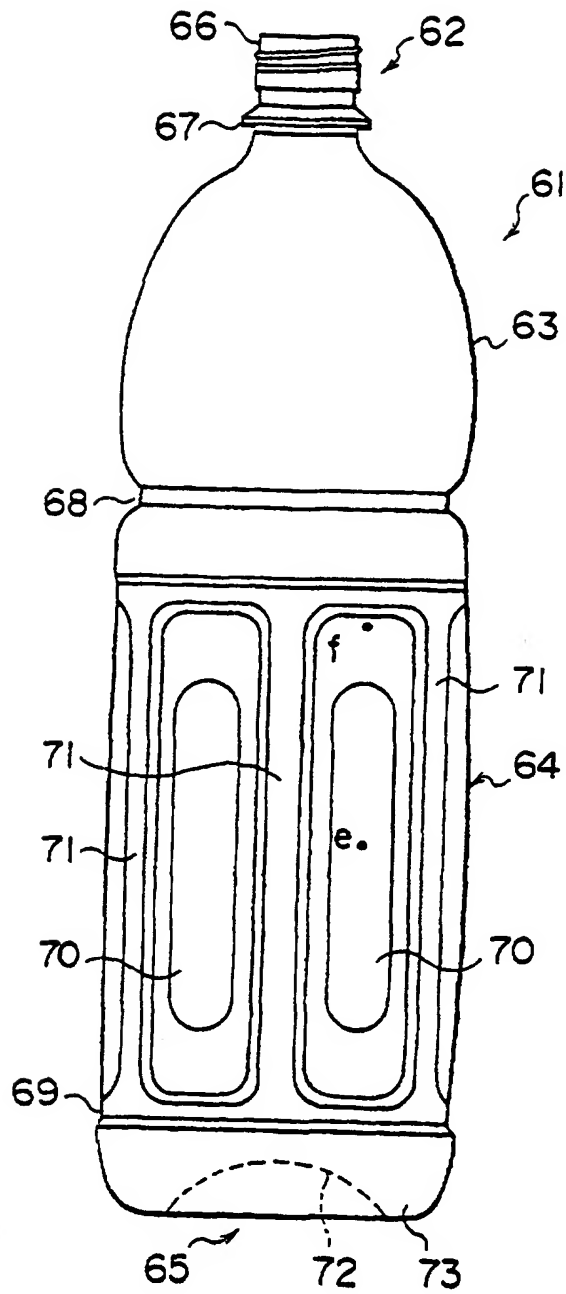
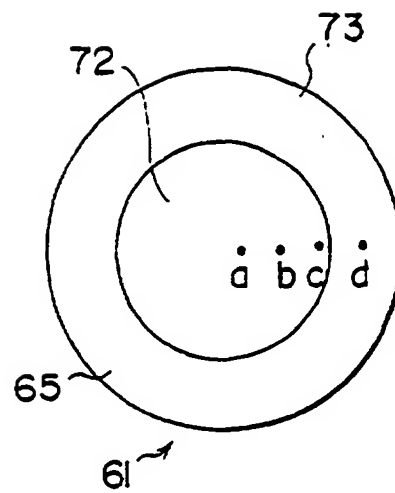


FIG. 12



THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)